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RETENTION WHEN USING A RETENTION AID**

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# THE INFLUENCE OF ALUMINUM SALTS ON FILLER RETENTION WHEN USING A RETENTION AID

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## ABSTRACT

An investigation was undertaken to understand further the interaction between aluminum salts and retention aids during papermaking. Retention experiments were performed on an apparatus designed to simulate the turbulent mixing and short polymer adsorption times found on a paper machine. The pH, aluminum concentration, and aluminum salts were varied in order to adsorb different types and amounts of aluminum species. In all cases, the presence of aluminum was found to be detrimental to polymer adsorption and filler retention. At low pH values where only soluble aluminum species exist, the aluminum adsorption was quite low and a moderate amount of directly adsorbed polymer produced good retention. At higher pH values, where the aluminum precipitated, the aluminum adsorption increased greatly. The aluminum precipitate from two different aluminum salts, aluminum chloride and aluminum sulfate, had varied effects on the polymer adsorption and filler retention. The observed trends are discussed and mechanisms are proposed.

## KEYWORDS

Adsorption, Alum, Aluminum salts, Polymers, Polyelectrolytes, Retention, Titanium dioxide, Wet end additives

## INTRODUCTION

The interaction of aluminum salts with retention aids has generally not been well understood because of the complex aqueous chemistry of the aluminum ion. Work by Hayden and Rubin (1) has produced a better understanding of aqueous aluminum chemistry and has provided a basis for the study of aluminum adsorption by cellulosic fibers by Arnson (2) and the evaluation of the influence of aluminum adsorption on polymer adsorption by Crow (3). The objective of this study was to build on Crow's work and investigate the influence of aluminum salts on polymer adsorption and filler retention.

In order to accomplish this objective, retention experiments were performed with varying pH values, aluminum concentrations, and aluminum salts. These factors influenced the type and amount of aluminum adsorbed, which in turn influenced the polymer adsorption and filler retention. Details of this study are available in Proxmire's thesis (4).

## EXPERIMENTAL

### Materials

A furnish of cotton linters pulp and 10% (based on o.d. pulp) anatase titanium dioxide was used in the retention experiments. A refined, fines-free, oxidized cotton linters pulp was used in order to minimize any interference from hemicelluloses,

lignin, or fines. The titanium dioxide had a larger than normal average particle size of 4.2 microns. The larger particle size was necessary to correctly measure the aluminum and polymer concentrations in the drainage samples. Aluminum chloride and aluminum sulfate were used as the sources of aluminum. Stock solutions of approximately 0.3M aluminum were prepared, filtered, and gravimetrically measured. Dilute aluminum solutions were prepared fresh daily from the stock solutions as needed. A commercial, high molecular weight, low-charge density, cationic polyacrylamide was used as the retention aid in this study. A polymer stock solution of 1000 mg/L was used to prepare the dilute polymer solutions just prior to the retention experiments.

## Apparatus

The apparatus used in this study was designed to simulate a papermaking system. As diagramed in Fig. 1, it consists of (1) a furnish delivery system, (2) a polymer delivery system, (3) a mixing tee, (4) a dynamic drainage jar, (5) a sampling section, and (6) a controller. The apparatus was designed so that the polymer would be rapidly and uniformly mixed with the furnish before entering the modified dynamic drainage jar. The dynamic drainage jar was used to simulate retention conditions found on a paper machine. The drainage jar had a 90 x 95 mesh plastic wire and was agitated at 1000 rpm. The sampling section divided the drainage sample into two parts. The first part was immediately filtered through a 2.0 micron pore size filter to separate the unretained furnish from the unadsorbed aluminum and polymer. The second part of the drainage sample was collected in a beaker and later used to measure titanium dioxide retention and zeta potentials.

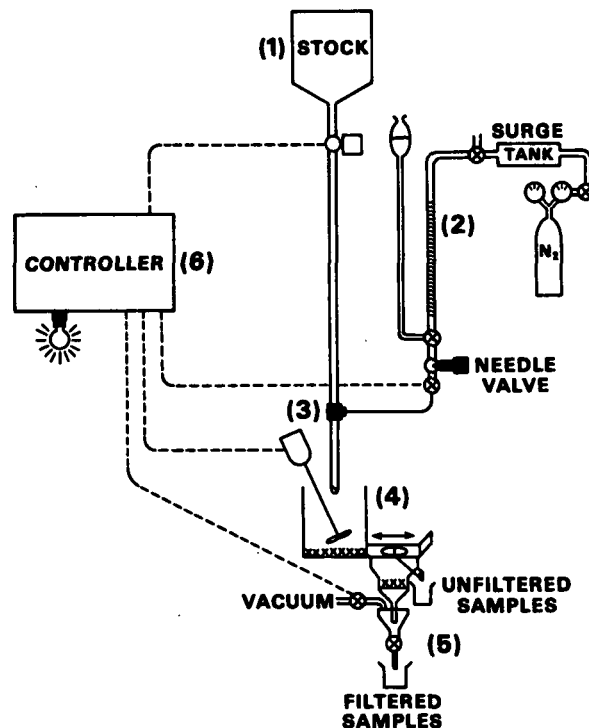


Fig. 1. Schematic of experimental apparatus.

In order to minimize the adsorption losses of additives, the apparatus and labware used in this study were made of Teflon, polypropylene, polyvinyl chloride, and polymer-treated glassware.

## Procedures

A basic retention run consisted of adding to a furnish of 1.5 g cotton linters and 0.15 g titanium dioxide in 450 mL of distilled water the following: (1) a KCl ionic strength background of 0.01N, (2) 0.01N HCl to adjust the pH to 3.9, (3) the aluminum salt, (4) 0.05N NaOH to adjust and maintain the pH at the desired value, and (5) distilled water to a total volume of 500 mL. The aluminum was allowed to adsorb at the desired pH for ten minutes. The furnish was then run through the retention apparatus where polymer was added and allowed to adsorb under turbulent conditions for 15 seconds. Drainage samples were then obtained and analyzed for zeta potential, titanium dioxide retention, aluminum adsorption, and polymer adsorption.

Zeta potentials of the drainage samples were determined by microelectrophoresis measurements using a Model B Zeta Meter.

Titanium dioxide retention was determined by filtration and ashing of 50 mL of the drainage samples.

Aluminum adsorption was determined by measuring the unadsorbed aluminum in the filtered drainage samples. This was determined spectrophotometrically at 450 nm by chelation of the aluminum with 8-hydroxyquinoline and extraction into methyl isobutyl ketone.

Polymer adsorption was determined by measuring the unadsorbed polymer in the filtered drainage samples. The polymer measurement was performed using a modified colloid titration technique. The principle behind the colloid titration technique is that a cationic polymer can displace a cationic dye from an anionic polymer. By measuring the amount of cationic dye released from a standard concentration of cationic dye-anionic polymer complex, the polymer concentration can be measured. The cationic dye, o-Toluidine Blue, and the anionic polymer, potassium polyvinyl sulfate, were used for this procedure.

A problem with this procedure was that the cationic aluminum species also react with the dye-polymer complex. It has been shown that maltol (3-hydroxy-2-methyl 4-pyrone) will complex with aluminum (5). Incorporating this reagent in the procedure permitted the polymer measurements to be made. As shown in Fig. 2, a varying effect was still observed depending upon the initial aluminum concentration; however, since aluminum concentrations were also measured, it was easy to correct for this interference. This procedure was accurate to within 0.1 mg/L for the polymer concentrations used in this study (0.0 to 3.0 mg/L).

## RESULTS AND DISCUSSION

### Aluminum Adsorption

The aqueous chemistry of aluminum is quite complex.

Using Hayden and Rubin's equilibrium constants, Arson found that aluminum chloride produces four aluminum species in the typical acid papermaking pH range of 4.0 to 5.5 (Fig. 3). The distribution of aluminum species for aluminum sulfate is more complicated than that of aluminum chloride. Because the sulfate ion can complex with the aluminum, sulfate ions are incorporated into the aluminum precipitate and polynuclear species. Crow found that the aluminum adsorption could be divided into two regions by the pH at which the aluminum starts to precipitate (pHp). Below the pHp there is low aluminum adsorption, while above the pHp aluminum adsorption increases substantially.

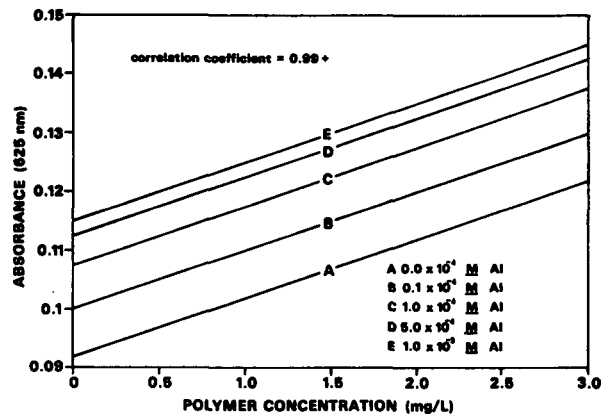


Fig. 2. Polymer concentration measurement using a modified colloid titration technique.

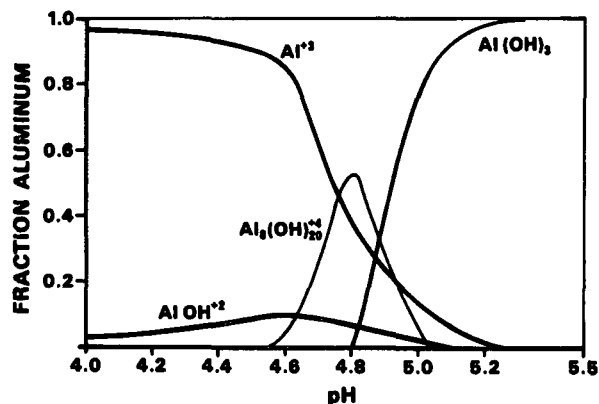


Fig. 3. Distribution of aluminum species as a function of pH for aluminum chloride ( $2.5 \times 10^{-4}$  M Al) (2).

Aluminum concentrations of 0,  $2.5 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$ , and  $10.0 \times 10^{-4}$  M were used in this study; at a pulp consistency of 0.3%, this corresponds to alum additions of 0, 50, 100, and 200 lb/ton, respectively. The aluminum adsorption for aluminum chloride and aluminum sulfate during the retention experiments is shown in Fig. 4 and 5. For reference, Crow's pH of precipitation values for the aluminum salts are included. In accordance with Crow's findings below the pHp where only soluble aluminum species exist, the aluminum adsorption is very low; above the pHp where the aluminum precipitate is formed, the aluminum

adsorption increases and becomes rather large. Because of its high concentration and high charge density, the trivalent aluminum ion is most likely the major adsorbing species below the pHp. Above the pHp, the deposition of aluminum precipitate accounts for the high aluminum adsorption.

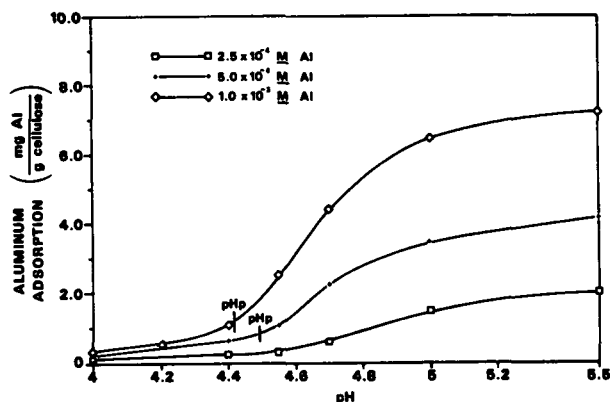


Fig. 4. The influence of pH and aluminum concentration on aluminum adsorption for aluminum chloride.

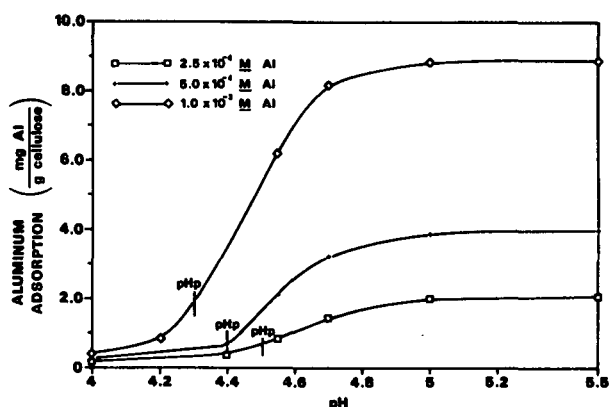


Fig. 5. The influence of pH and aluminum concentration on aluminum adsorption for aluminum sulfate.

Figures 4 and 5 also show that increasing the aluminum concentration increases the aluminum adsorption and lowers the pHp. Also, above the pHp the aluminum adsorption is greater for aluminum sulfate than for aluminum chloride. With both salts the aluminum precipitate is positively charged up to pH 8.5-9.0 due to the adsorption of cationic aluminum species (6,7); however, with aluminum sulfate the complexing nature of the sulfate ion reduces the cationic charge of the precipitate (Fig. 6). This reduces the repulsion between adsorbed and unadsorbed aluminum and produces greater adsorption.

#### Polymer Adsorption

The influence of pH and aluminum concentration on polymer adsorption is shown in Fig. 7 and 8 for

aluminum chloride and aluminum sulfate, respectively. At all pH values the aluminum salts reduce polymer adsorption. At low pH values where the soluble aluminum species exist and the aluminum adsorption is low, both aluminum salts give moderate polymer adsorption. Increasing the aluminum concentrations results in decreasing the polymer adsorption. This indicates that there is a competition between the soluble aluminum species and the polymer for adsorption sites as would be expected in an ion exchange adsorption mechanism.

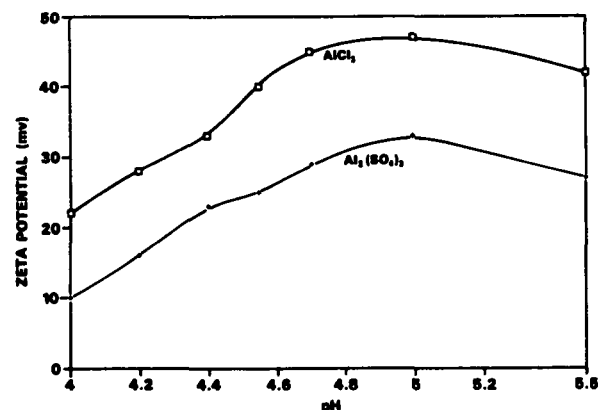


Fig. 6. The influence of pH and aluminum salt on the zeta potential of drainage samples ( $1.0 \times 10^{-3}$  M Al; 3.0 mg/L polymer addition).

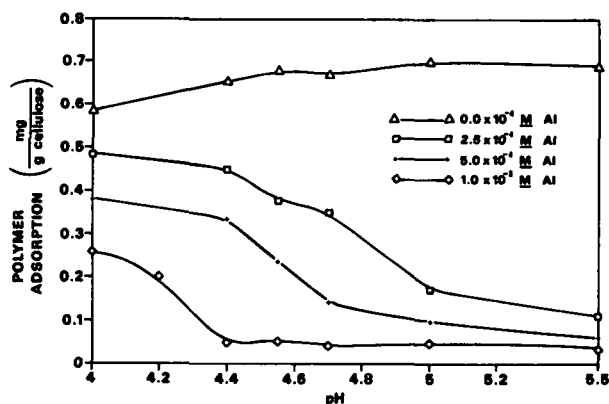


Fig. 7. The influence of pH and aluminum concentration on polymer adsorption for aluminum chloride (3.0 mg/L polymer addition).

At higher pH values where the aluminum adsorbs as a precipitate, the two salts produce different effects. The aluminum chloride precipitate reduces the polymer adsorption to low levels. This is because the precipitate creates a highly cationic surface on the furnish which repels the cationic polymer. With the aluminum sulfate precipitate a decrease in polymer adsorption is not observed, even though more aluminum precipitate is adsorbing. Like the aluminum chloride precipitate, the aluminum sulfate precipitate also creates a cationic surface on the furnish which would be expected to repel the cationic polymer. However,

at the low aluminum concentration the polymer adsorption is approximately constant, and increasing the aluminum concentration increases the amount of polymer adsorbed. The major difference between the two aluminum precipitates is that aluminum sulfate precipitate has sulfate ions incorporated into it and the aluminum chloride precipitate does not. The screening of cationic charges by the sulfate ions cannot fully account for the differences in polymer adsorption. The sulfate ions in the precipitate must act as additional adsorption sites for the polymer.

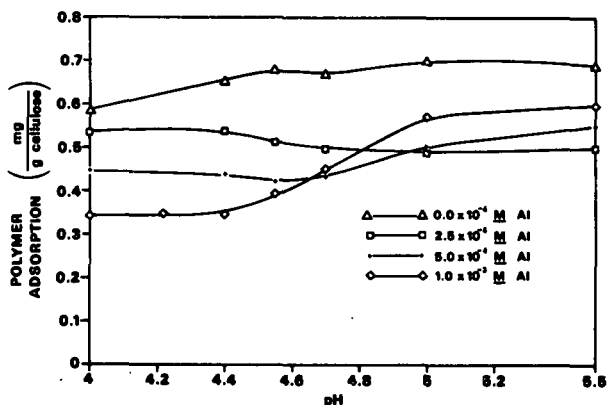


Fig. 8. The influence of pH and aluminum concentration on polymer adsorption for aluminum sulfate (3.0 mg/L polymer addition).

#### Titanium Dioxide Retention

The influence of pH and aluminum concentration on titanium dioxide retention is shown in Fig. 9 and 10 for aluminum chloride and aluminum sulfate, respectively. The filler retention generally follows the polymer adsorption trends. For aluminum chloride the best retention is at low pH values where there is moderate, direct polymer adsorption and low zeta potentials. As the pH is increased, the furnish becomes covered with a cationic aluminum precipitate which increases the furnish surface charge, reduces the polymer adsorption, and decreases the filler retention.

For aluminum sulfate at low pH values, there is a moderate amount of directly adsorbed polymer and low zeta potentials which result in good filler retention. Initially as the pH increases, the retention decreases. This probably is due to increasing zeta potentials and the screening effects of the soluble aluminum species. With further increases in pH the retention values increase. The leveling off of zeta potentials, the decrease in soluble aluminum species, and the increase in polymer adsorption can all contribute to the increase in retention. Even though there may be higher polymer adsorption at the high pH values, the filler retention is less than that at the low pH values because of the higher zeta potentials and weaker polymer bonds.

#### Mechanisms

In order to understand how the polymer adsorbs, scanning electron micrographs were taken to see how

the aluminum precipitate was adsorbing. Figure 11 shows a clean fiber surface and Fig. 12 shows a fiber with precipitated aluminum on its surface. The aluminum precipitate covers a large portion of the fiber surface. Therefore, the polymer is probably adsorbing to the precipitate instead of directly to the fiber surface.

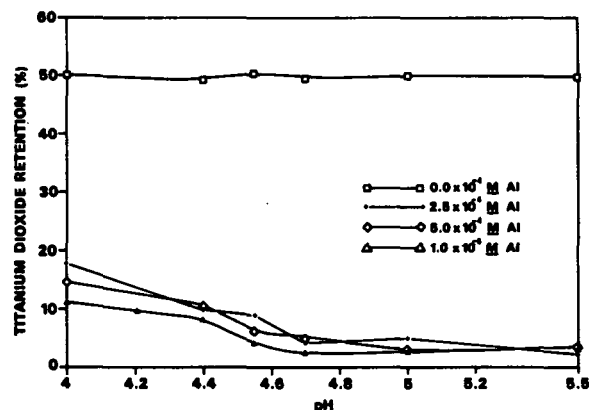


Fig. 9. The influence of pH and aluminum concentration on titanium dioxide retention for aluminum chloride (3.0 mg/L polymer addition).

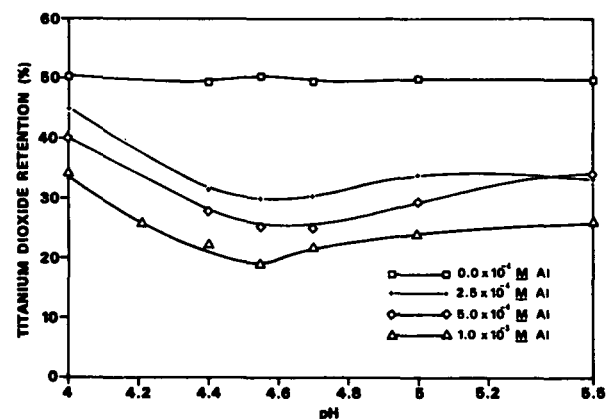


Fig. 10. The influence of pH and aluminum concentration on titanium dioxide retention for aluminum sulfate (3.0 mg/L polymer addition).

Retention experiments were performed at varying degrees of agitation to see how effective the polymer was in the different pH regions. Figure 13 shows that the titanium dioxide retention trends varied between the low and high pH regions at the various agitation levels. The aluminum adsorption and polymer adsorption curves were very similar at the different agitation levels. In the low pH region, the titanium dioxide retention curves showed similar trends with better retention as the degree of agitation decreased. However, in the upper pH region, various retention trends were observed. At the low agitation level, there was a large increase in retention. At the medium agitation level, there was a moderate increase in retention; and at the

high agitation level, there was a decrease in retention. This indicates that the polymer bonding in the upper pH region is rather weak, as would be expected if the polymer were adsorbing onto the aluminum precipitate instead of directly to the fiber surface.



Fig. 11. Electron micrograph of clean fiber surface.



Fig. 12. Electron micrograph of fiber surface covered with aluminum precipitate from aluminum sulfate ( $1.0 \times 10^{-3} \text{ M Al}$ ; pH 5.5).

Aluminum precipitate desorption experiments also were conducted to determine where the polymer was adsorbing. Retention experiments were performed in the usual manner, except that after the polymer was adsorbed, the aluminum precipitate was desorbed by acidification. Polymer which had been adsorbed to the aluminum precipitate would also desorb. A cationic surfactant, cetyltrimethyl ammonium bromide, was added immediately before acidification to prevent readorption of the desorbed polymer onto the newly exposed surfaces. The polymer adsorption results in the presence of the

surfactant alone and the surfactant plus acid are shown in Fig. 14. When the surfactant was added without acidification, a typical polymer adsorption curve was obtained, indicating that the surfactant has no significant effect on the adsorbed polymer. When the surfactant was added and the slurry was acidified, similar polymer adsorption values were obtained in the low pH range, but the polymer adsorption substantially decreased in the high pH range. The difference between the two curves indicates the amount of polymer adsorbed onto the aluminum precipitate. Therefore, in the low pH region the polymer adsorbs directly to the furnish surfaces; but in the high pH region, a large portion of the polymer is indirectly adsorbed by adsorbing onto the aluminum precipitate.

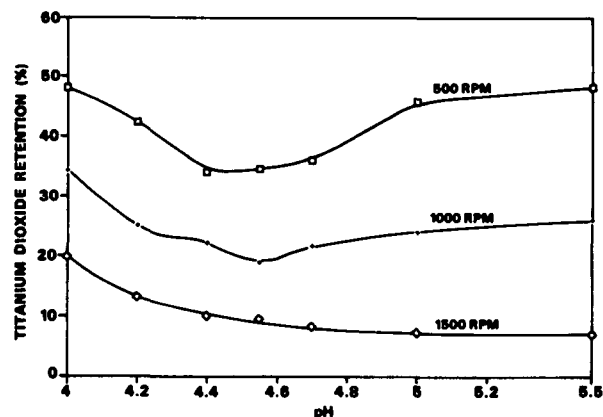


Fig. 13. The influence of pH and agitation rate on titanium dioxide retention for aluminum sulfate ( $1.0 \times 10^{-3} \text{ M Al}$ ; 3.0 mg/L polymer addition).

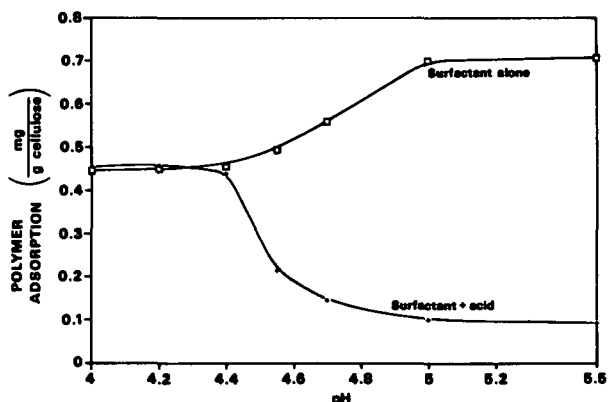


Fig. 14. The influence of aluminum precipitate desorption on polymer adsorption ( $1.0 \times 10^{-3} \text{ M Al}$  from aluminum sulfate; 3.0 mg/L polymer addition; 1 minute polymer contact time).

## CONCLUSIONS

A knowledge of aqueous aluminum chemistry is necessary to understand how aluminum salts affect polymer adsorption and filler retention. At low pH values only soluble aluminum species exist and

aluminum adsorption is low. In this region the polymer was found to be directly adsorbed to the furnish surface and to be in competition with the soluble aluminum for adsorption sites. A moderate amount of directly adsorbed polymer and low zeta potentials produced moderate retention levels.

At high pH values the aluminum salts precipitated and produced high aluminum adsorption. With aluminum chloride the furnish became coated with the highly cationic aluminum precipitate, which repelled the cationic polymer and resulted in low filler retention. With the aluminum sulfate the furnish also became coated with the cationic aluminum precipitate but had a lower charge due to the incorporation of sulfate ions into the precipitate. The polymer was found to adsorb to the aluminum precipitate. Increasing the aluminum concentration in this pH region increased polymer adsorption. Even with higher polymer adsorption, the filler retention did not increase above the low pH values. This is due to the higher zeta potentials and weaker nature of the polymer bond when the polymer is bonded to the aluminum precipitate instead of directly to the furnish surface.

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